

---

# Renewable Fuels and Materials

JOHN PIERCE  
*DuPont*  
*Wilmington, DE*

I'll give my views on how I see the evolving fuels and materials areas, but I'll start with a historical perspective with some slides used in 1996 in discussions with upper management at DuPont on why we ought to focus on bioproducts. Enormous quantities of materials are available from agriculture and though prices fluctuate over time, they're cheap on a per-pound basis (Fig. 1). Supplies tend to exceed demand even though distribution is problematic. Biotechnology, of course, provides tools to start converting agricultural feedstocks into various types of materials.

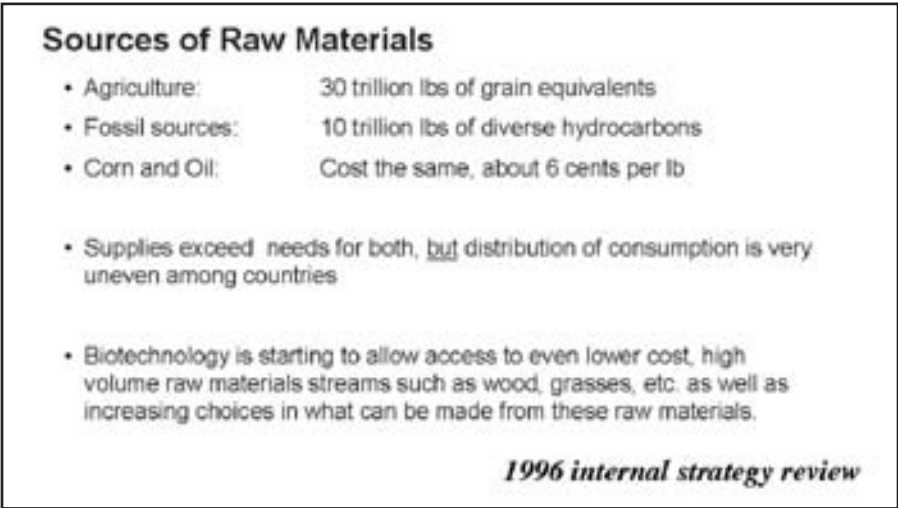


Figure 1. Sources and costs of feedstocks, 1996.

Figure 2 shows the relative price of corn versus oil. For most of last century, oil was cheaper on a unit-weight basis than corn. That has become less and less true. Today, even with corn prices at record highs, on a per-pound basis the corn versus oil ratio is at a historic low. This brings into focus the factors that can drive new processes and new feedstocks.

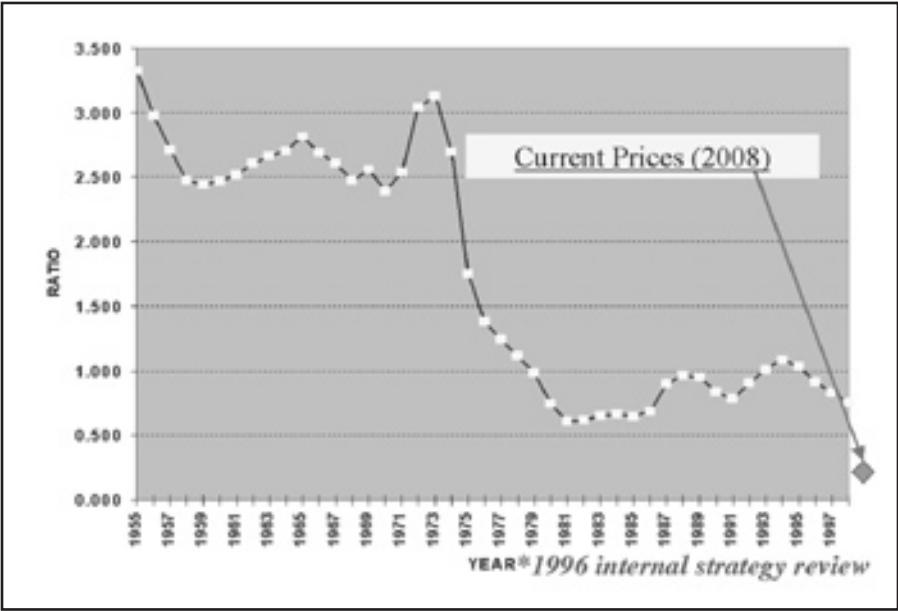


Figure 2. Price ratio, corn: oil (\$ per lb).

Historically, we’ve had two separate industries (Fig. 3). You had the folks like Dupont who take a barrel of petroleum and do some fancy chemical engineering with it and make a better thing for better living, such as a nice polymer. That continues to be important. The other group, who hardly interacted with the polymer side of the house, grew and sold raw agricultural materials for various purposes. And then along came biotechnology and the idea that you can start doing something purposeful with the products of agriculture, and the two groups started eyeing each other. We started understanding more about companies like ADM, Cargill and Tate & Lyle, and they started understanding more about the chemical industry.

At Dupont, this perspective caused us to look hard at what we were doing and to make commitments about our future (Fig. 4). I remember at the time our chairman announced the plans, I thought, “I don’t know how we’re going to do that.” However, we’ve made some strong moves in terms of sustainability. Now, most of these have been “mindset” related; once you decide you are going to be sustainable and renewable, you find all kinds of ways to achieve that. Some are agriculturally based and some are process-based involving normal chemical approaches.

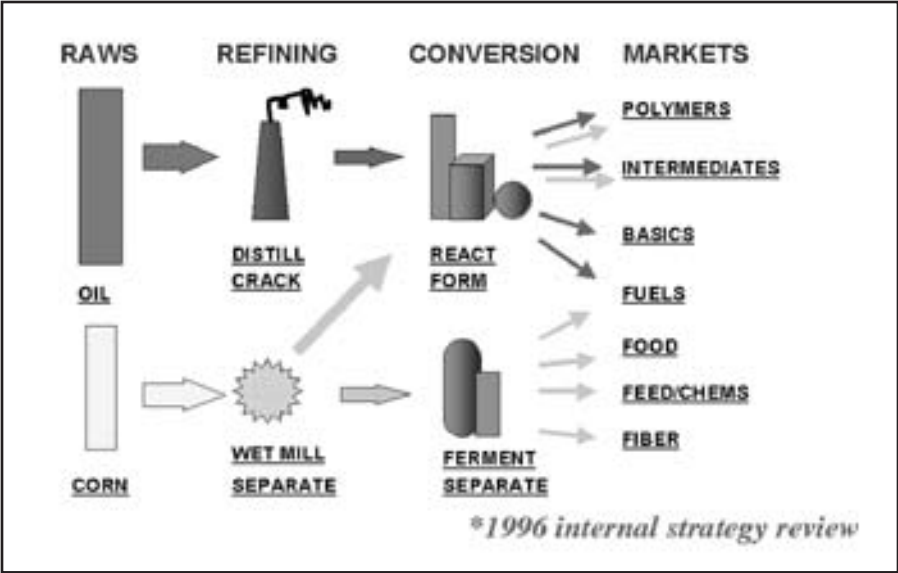


Figure 3. Two industries starting to partner and compete (1996).

2007 ANNUAL REPORT

**DUPONT**

- 25% of revenues from businesses not requiring depletable raw materials  
*18% achieved to date*
- 10% of energy needs derived from renewable sources  
*6% achieved to date*
- Energy flat vs 1990 and 65% reduction in equivalent greenhouse gas emissions  
*Energy down 7%; GHG down 72%*

Figure 4. DuPont's commitments by 2010.

# BIOBASED ECONOMY

Today we can convert agricultural feedstocks into intermediates like starch, cellulose and sugar and, with the appropriate enzymes and biocatalysts, convert these into chemicals, materials and fuels (Fig. 5).

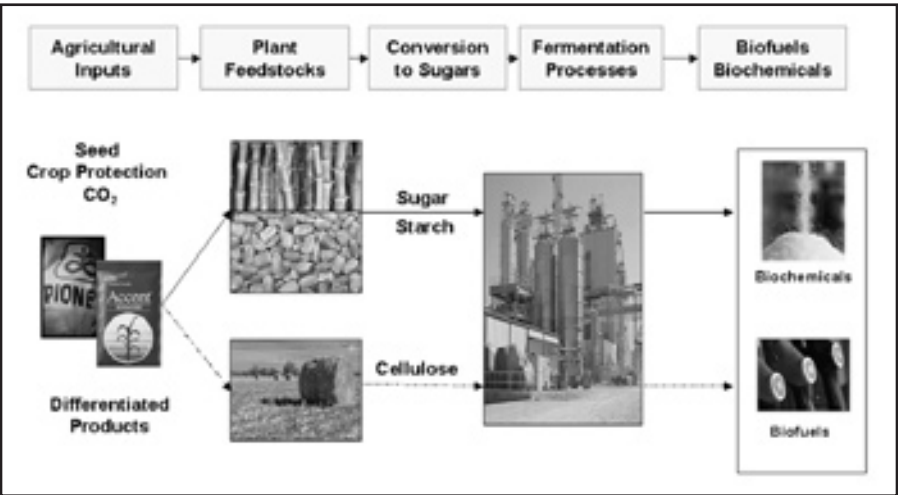


Figure 5. The biorefinery value chain, the foundation of the biobased economy: carbohydrates to fuels and chemicals.

Now, a few thoughts to bear in mind: it was one thing back in 1996 to say, “This is how it’s going to be,” but it was quite another thing to actually do something about it. This is a complex, large volume, long value-and-process chain. A lot of cost constraints are involved and everything must be kept in balance. Technology is complex; therefore, even though we are a large company with a long history of technological innovation, we also form partnerships to bring in various pieces of the puzzle. When you go into a new area you may have government incentives to get you over some of the humps, such as the famous “valley of death” between research and commercialization. However, I would make the point that proper thermodynamics *and* kinetics are required if you are going to be successful. You must have the right view of the picture, but there may be many paths to an end-point. Some of them may land you in jail and some will take you where you want to go.

## CONVERSION OF BIOMASS

What about biomass conversion today? Cornstarch plus enzymes make glucose, or you can use cane sugar. Processing comprises wet- and dry-grind corn mills in the United States, and cane-processing facilities in Brazil. Standard yeast conversions to ethanol occur at high volumes. Numerous other processes involve a variety of microorganisms—most of them are unimproved, some of them have been evolved and a few of them engineered—to make a variety of molecules. And, fundamentally, this takes advantage of existing infrastructure, to get raw materials to the plant.

Now, what might be the thermodynamically ideal system? It starts with high, sustainable yields of biomass per acre. At this conference, we'll hear more about new, high-yielding biomass energy crops. You want to use the things that are made all over the place. You don't want one-off facilities at each location. You don't want to have too much work with this material; you want flexibility. You want to minimize capital outlay and you want flexibility also in plant size. This is bread-and-butter manufacturing. The next questions is, "What's the best way to get there?"

#### NEW PLATFORM CHEMICALS

A few years ago, scientists at the National Renewable Energy Laboratory published a treatise on top value-added chemicals from biomass. The objective was to identify the intermediates to synthesize from complex biomass. Figure 6 lists those top sugar-derived building blocks—molecules that have end-groups and “handles” that chemists know how to work with and convert into other compounds—a very different group of chemicals from the corresponding top ten for the petrochemical industry, *i.e.* ethylene, propylene, *etc.* Maybe we could make other simple intermediates that could then be converted into more valuable things.

- **1,4 diacids (succinic, fumaric and malic)**
- **2,5 furan dicarboxylic acid**
- **3 hydroxy propionic acid**
- **aspartic acid**
- **glucaric acid**
- **glutamic acid**
- **itaconic acid**
- **levulinic acid**
- **3-hydroxybutyrolactone**
- **glycerol**
- **sorbitol**
- **xylitol/arabinitol**

Figure 6. Top sugar-derived building blocks.

We focused on a new three-carbon molecule called propanediol (PDO). Dupont had known since the 1940s that a wonderful polyester could be made from this. We could never find a way to make it cheaply enough from petroleum, so we started experimenting with biological approaches. We achieved it and embarked on a metabolic engineering program. It was a complex project to genetically engineer *E. coli* to convert glucose at high yields, high rates and high titers into propanediol. We learned that the complex metabolic engineering was possible and we also found that it was commercializable. Our first shipment of bio-PDO was delivered in late 2006. We are now beginning to match the technology with the feedstock. This process taught us is that it is possible to use biological raw materials to make heretofore inaccessible chemicals that have industrial applications.

MARKET ENTRY

Using the Porter model of competition (Fig. 7), I want to talk about what you *should* make. If you are making a new material like PDO, there is a high barrier to entry. If you

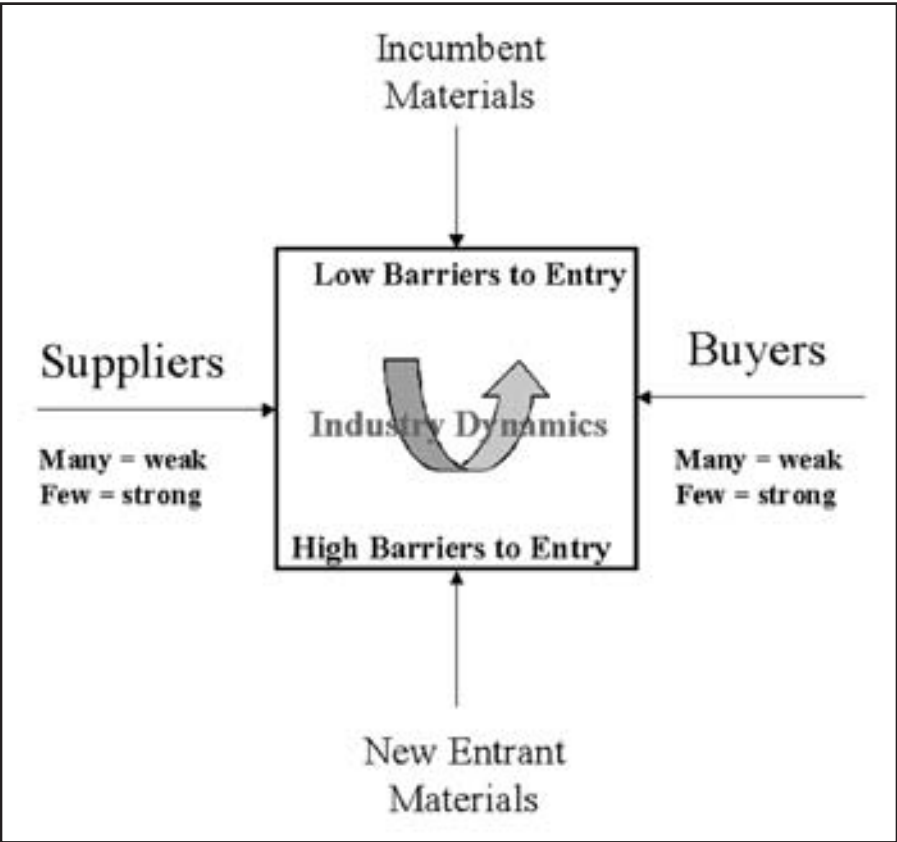


Figure 7. The Porter model of competition.

are making an incumbent material, the barrier to entry is low, and you have to decide if the market you are focusing on has many suppliers or many buyers. The choices you make determine whether it will be difficult or easy. Figure 8 shows idea-process steps for men's cotton slacks. Between the farm and the store, many people “touch” the item being purchased, each of whom must make a profit. It’s a complicated value chain, and to enter it you need to change something within it and you have to talk to a lot of people along the way to make that happen. It can be valuable if you can do that, but it’s not simple.

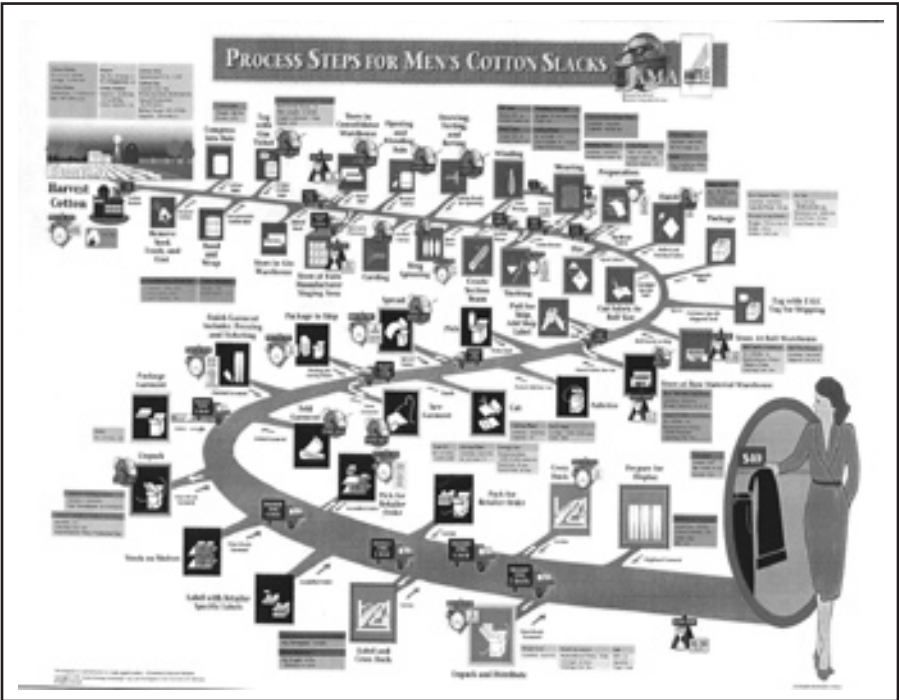


Figure 8. The complicated process of manufacture and delivery of cotton slacks.

The polymer we make—Sorona® (Fig. 9)—has utility in fabrics. I have a suit made of a wool blend and, again, if you track that PDO from Tennessee, a complicated process led to it getting into that suit. By comparison, the North American carpet industry is simple; the polymer comes in and the carpet goes out (Fig. 10). Within such a concentrated industry, those involved care a lot about price and performance, *etc.*, so you have to be very careful to supply the right materials. So, here we have the same product, but two very different value chains.

In a highly fragmented many-step value chain with many decision-makers along the way, it can take a long time for a new technology to diffuse through it. With the carpet example, if you make the right sale, you may quickly induce a major change in the market and soon be running to keep up with demand; can you make the polymer fast enough?

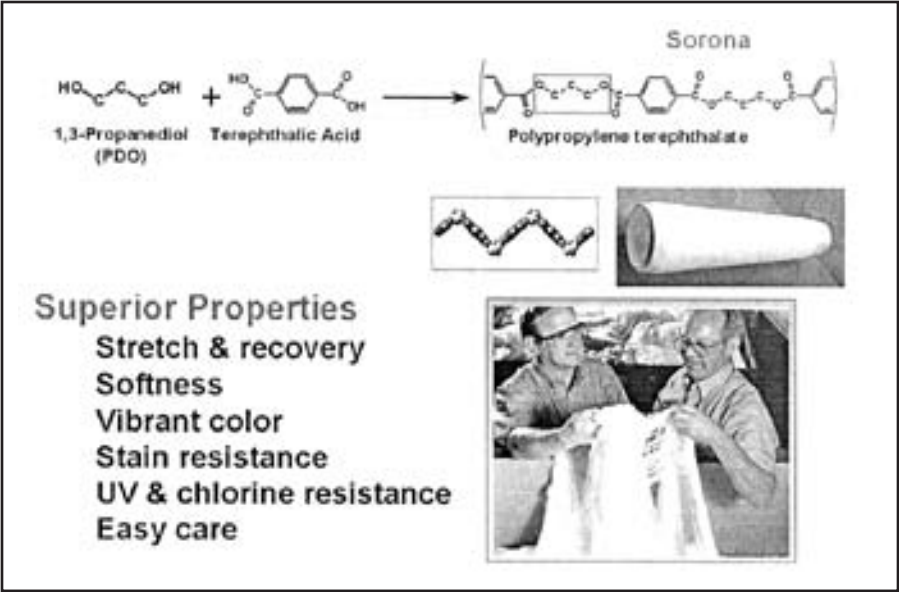


Figure 9. Sorona®: an advanced polymer/fiber.

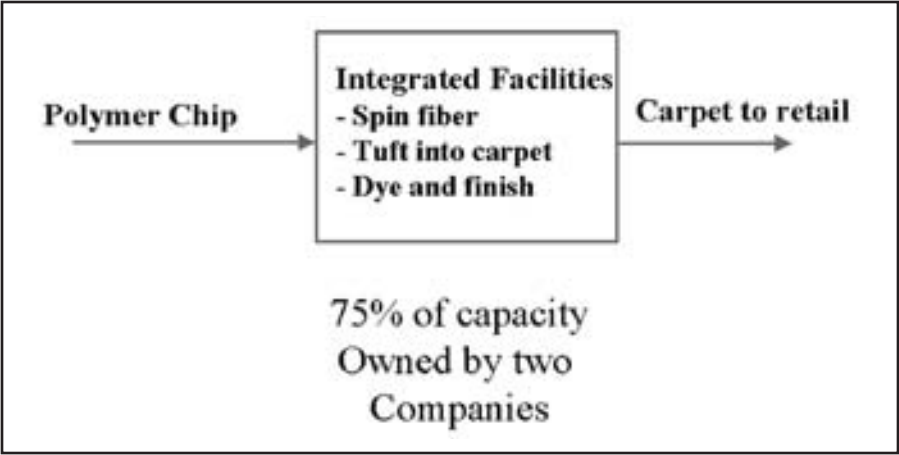


Figure 10. Structure of the North American carpet industry.

All you need is one “yes” from a particular person and you may soon need to expand capacity. Those two very different worlds can result from the same innovation.

What shall we make? With an existing material or chemical you have low market risk, but price is paramount. In our experience, there is generally lower capital intensity and you can get profitability at smaller scale with biological processes than with chemical processes. So that can be a helpful thing, depending on the market. With a new mate-



rial or chemical, you have a high market risk. You have to explain to the market how it works. It's a significant technological risk especially if the only way to make this material is biologically and you can't make a little chemically to test the market. Then you have much high-risk R&D before you have enough material to fully test your hypothesis. And you need to offer the new attributes at the right price. One thing to consider with a new chemical, is extending existing markets through lower-cost routes especially for a medium-volume chemical. You can get higher margins if you can reduce cost. You have life-cycle-analysis benefits and environmental benefits. As mentioned, there is often an advantage in the biological approach at the smaller scale. You can build more quickly than if you have to wait until the demand is sufficient to justify building a large petrochemical plant. But this requires integrated science and collaboration among people who normally don't interact.

I don't have a list of the molecules to make, but if you have any, call me. Deciding what molecule to make is the single most important thing. The second most important consideration is what feedstock to use, and the third most important decision is the biocatalyst. If you have any ideas—I'm serious—please be in touch.

## BIOFUELS

Biofuels have elicited enormous interest around the world. There are aspects of greed, politics, national security, economics and environment—there's an issue for everyone—which is partly why it has garnered so much attention. Biofuels are *the* alternative to liquid transportation fuels, almost all of which come from petroleum, whereas several options exist in the other areas for stationary power or electricity.

The power density with biofuels fits well with the current infrastructure. There's an enormous market, and it's growing (Fig. 11). How many hundred-million-gallon facilities will need to be built at \$200 million per facility, to get to these enormous numbers? It's a huge undertaking.

Venture capitalists are funding new technologies. The Department of Energy has established three large centers to examine a variety of approaches. With oil at \$140 a barrel, technologies that hitherto were not competitive then look interesting. There are chemical approaches, thermochemical approaches and biological approaches, all of which are being developed. Scores of companies and institutions are trying various technological permutations to make biofuels. From our perspective, the current biofuel solutions are inadequate to address needs, and our approach is to work on:

- higher-yielding feedstocks through our Pioneer subsidiary, and
- alternative fuels that fit well with current infrastructure.

We are big believers in products that work in existing infrastructure. When a society spends billions of dollars to establish an infrastructure, you must take it into account. Although infrastructures do change, they change slowly. This isn't "dot com" stuff. Such change is a real-world, heavy-lifting activity.

Our cellulosic ethanol method is a standard mill / pretreat / saccharify / ferment / separate process, but making it work requires utmost integration. We recently established a joint venture with Genencor to help achieve this integrated activity and we look for-



Figure 11. Biofuels: a high-volume, high-growth market (billions of liters and compound annual growth rates for 2007–2020).  
The 2020 market is projected at >\$200 billion.

ward to having a commercial process in the near future. Again, regarding infrastructure, we intend to pay attention to the many plants that are already sited in prime farming locations. Currently, they take corn grain and grind it—either wet or dry—and make glucose. From a standard yeast fermentation, they make ethanol. Right next door, we'll erect a cellulosic facility that will take the waste parts of the corn plant to produce more ethanol as well as PDO (Fig. 12). Our analyses suggest that we can take off about 50% of the stover for our process without affecting soil fertility. On some soils you can take more, and on others you can take less. The process on the right of Fig. 12, turns the mix of sugars into ethanol. The current “waste” products of the wet- and dry-mill processes become further substrates for the cellulosic side and enough energy is left over from the lignin and other unfermented materials to energize the whole process. Figure 13 provides a representation of the fermentation process. We use a strain of the bacterium *Zymomonas mobilis*, manipulated to co-ferment five- and six-carbon sugars. We get high titers of ethanol; essentially all of the five- and six-carbon sugars are converted to ethanol. We still want to move the xylose line in Fig. 13 a little to the left to complete the fermentation more quickly. And we need to improve sugar production, which is why we've entered the joint venture with Genencor.

### BIOBUTANOL

Biofuels are more than just ethanol and biodiesel. Ethanol and biodiesel are important because their production technologies have been available for some time. Yeasts have been used for a long time to convert glucose to ethanol, and people have been saponify-

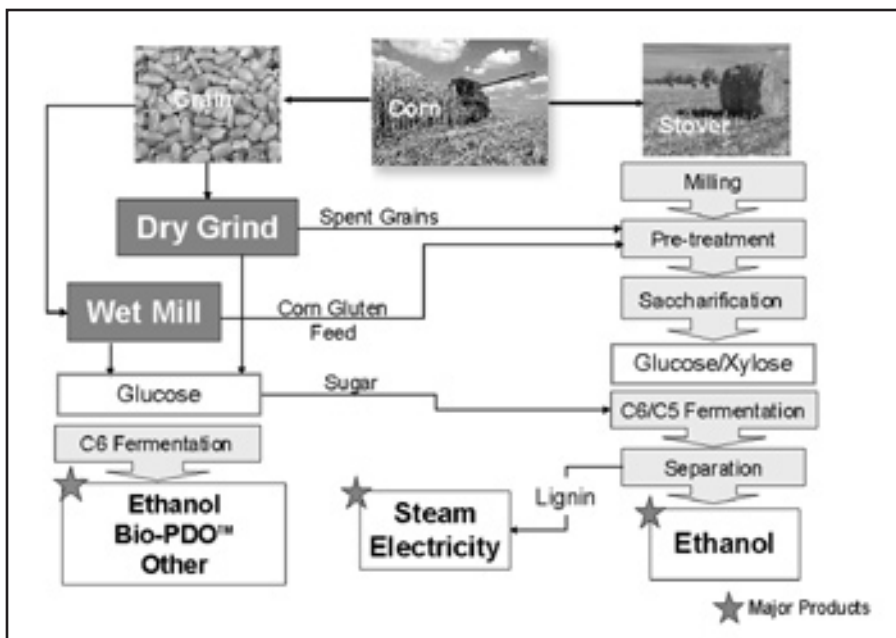


Figure 12. The integrated corn biorefinery.

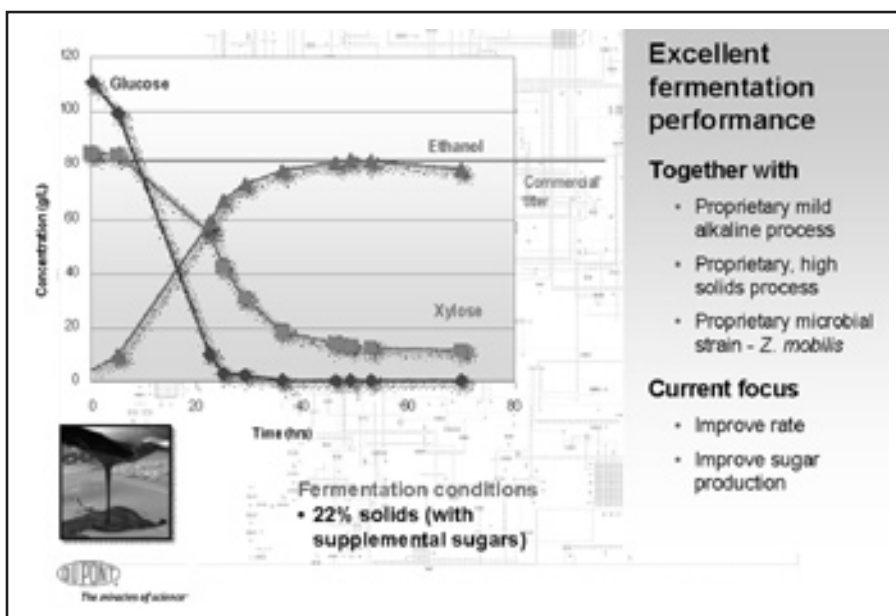


Figure 13. Fermentation performance of genetically engineered *Zymomonas mobilis*.

ing fats for a long time. A number of companies are trying to use thermochemical and biochemical technologies, to make various kinds of materials. Some years ago, we sat down with BP representatives to try to figure out an optimal space in which to operate: what are good fuel properties versus what is achievable biologically? We came up with biobutanol, which has several good features. It can be blended completely flexibly. You can run it through pipelines and it gives more miles per gallon. Also, importantly, it helps ethanol use—it's not an either-or situation with respect to ethanol. With a little butanol in the gas tank you can add more ethanol and keep the vapor pressure down. Thus, it contributes to current infrastructure.

The Weizmann process for butanol synthesis has been available for many years, named after the first president of Israel. This natural so-called ABE process produces acetone, butanol and ethanol (Fig. 14). Although used commercially around the world, it is not economical as a fuel. Our approach has been to make butanol for transportation use. There are four isomers, all of which have good fuel values: high energy density, easy to blend, and less corrosive than ethanol. We have been working on iso-butanol and 2-butanol, which have higher octane values than normal butanol (Fig. 15), using biochemical techniques to engineer pathways into microbes and we've been able to produce microbes that can convert glucose into either butanol or isobutanol or 2-butanol. We're working to increase the rates, titers and yields so they can be competitive. We have exceeded the ABE commercial standard, but wish to do better before declaring success.

I suggested the need to have thermodynamics and kinetics on your side. So, what might be a kinetically feasible path? Again, my belief is that improved corn and sugar-cane yields will continue to make these crops important for years to come. Other kinds of energy

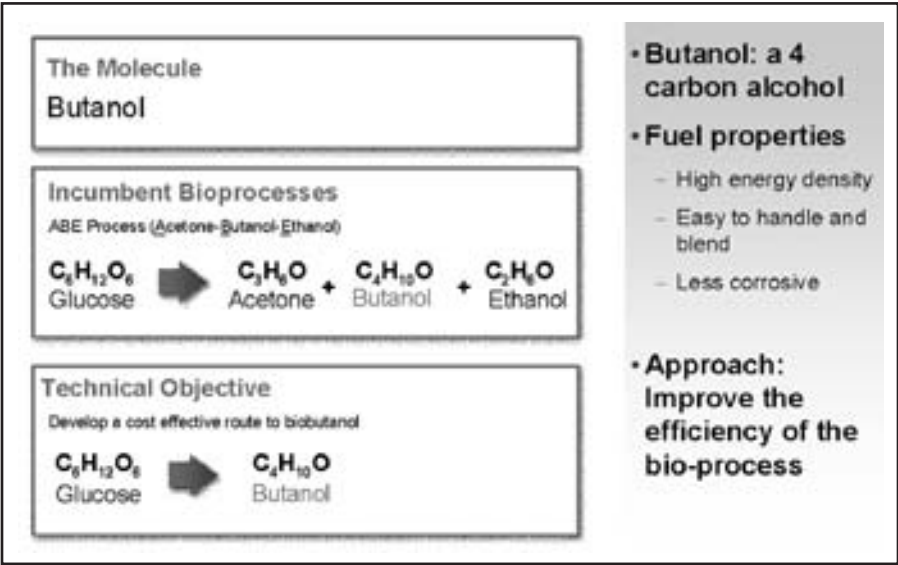


Figure 14. Biobutanol.

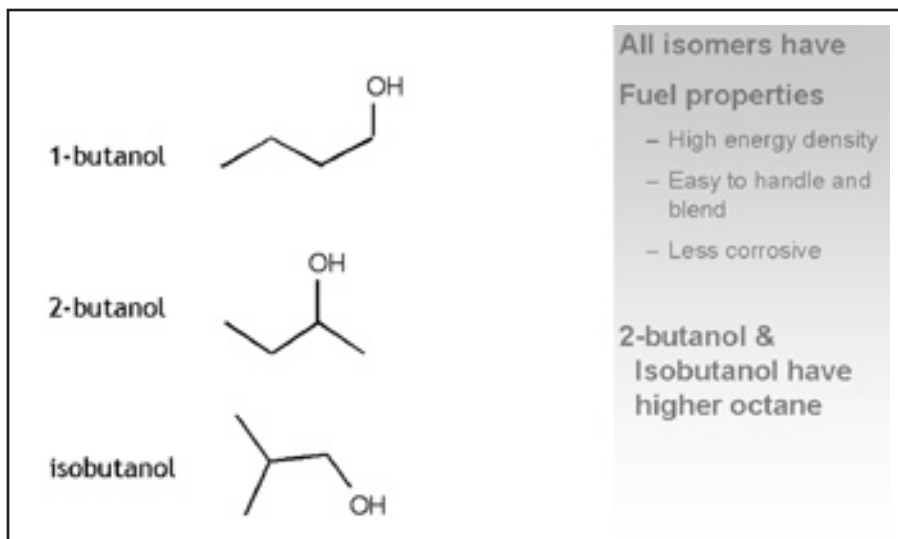


Figure 15. Isomers of butanol.

crops—high-yielding biomass feedstocks—will also be important. Approximately 90 million acres of corn were planted in 2007 in the United States, and every year there are likely to be yield increases of a few percent. Processing improvements will foster movement to significant production of cellulosic-based biofuels over the next 10 years. We'll start seeing cellulosic facilities this year, next year and the year after, but it will take several years before those volumes are significant. Breeding for biomass will redefine harvestable yield, both in standard crop plants and energy crops. Existing ethanol-production plants will initially be retrofitted to take advantage of their prime locations and synergies between current and future processes. We're getting better at making the biocatalysts and integrating biocatalytic processes and we will continue to set the pace for innovation. We will have the ability to produce microbes that synthesize many different types of molecules. It's getting faster and faster. What used to take 10 years now takes 8 and a little while from now it will take 6. We are on a steep learning curve with this technology.

### INTEGRATION IS KEY

It's not just about biotechnology and it's not just about fuels. It really is all based on agriculture and if you take the three ratios in Fig. 16 and multiply them by each other, you get revenue per land area. There's a finite area of land and you need to maximize the revenue from it. To do that, you need to have all the tools in hand for agriculture, engineering, chemical engineering and distribution and you also have to make sure you don't fail once you have made the product and now you are trying to market it. It's complicated but exciting to contemplate.

Integrated approaches are necessary, partnerships are essential and you have to make sure that you are working on the right thing and in the right fashion.



Figure 16. Critical success factors.



**JOHN PIERCE** is vice president of technology at DuPont Applied BioSciences, with responsibility for DuPont's biotechnology R&D efforts in the production of fuels, chemicals and materials. He began his career at DuPont in 1982 as a research scientist in Central Research & Development (CR&D). He moved to agricultural products in 1988 and held research-management positions in agricultural biotechnology and in crop-protection chemical discovery. In 1994, he became director of chemical and biological sciences in CR&D, where DuPont's current focus on industrial biotechnology began to take shape.

From 1996 to 1998, Dr. Pierce was based in Paris as planning manager for agricultural products for Europe, the Middle East and Africa. Upon returning to Wilmington, he worked to integrate the agricultural biotechnology research efforts of DuPont and its subsidiary Pioneer Hi-Bred International. In 2001, he returned to CR&D as director of biochemical sciences and engineering and was named to his current position in June 2006.

He is a founding board member of the Society of Biological Engineering and serves as a member of the Department of Energy's Biological and Environmental Research Advisory Committee. He has a BS degree from Penn State and a PhD from Michigan State University.